

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-292741

(43)Date of publication of application : 15.10.2003

(51)Int.Cl.

C08L 67/00  
C08G 81/02  
// (C08L 67/00  
C08L 23:26 )

(21)Application number : 2002-099859

(71)Applicant : NIPPON PETROCHEMICALS CO LTD

(22)Date of filing : 02.04.2002

(72)Inventor : TAKASHIMA TSUTOMU  
INOUE TOSHIO

## (54) POLYESTER RESIN COMPOSITION REINFORCED WITH INORGANIC FILLER

## (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a polyester resin composition reinforced with an inorganic filler and having excellent strength and hydrolysis resistance.

SOLUTION: This polyester resin composition reinforced with the inorganic filler is produced by melting and kneading 95-55 pts.wt. of a thermoplastic polyester resin, 5-45 pts.wt. of an inorganic filler (the sum of the resin and the filler is 100 pts.wt.) and 0.1-5 pts.wt. of a liquid polybutene having an epoxy group on the terminal.

## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

## \* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

 CLAIMS
 

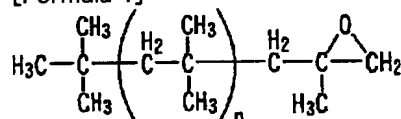
---

[Claim(s)]

[Claim 1] The inorganic bulking agent consolidation polyester resin constituent obtained by carrying out melting kneading of the liquefied polybutene 0.1 which has an epoxy group at thermoplastic polyester 95 - 55 weight sections, an inorganic bulking agent 5 - 45 weight sections (the 100 in all weight section of both is carried out.), and the end - the 5 weight sections.

[Claim 2] The inorganic bulking agent consolidation polyester resin constituent according to claim 1 characterized by more than 80 mol % of the liquefied polybutene which has an epoxy group at the end being what has the structure of a formula (1).

[Formula 1]



式(1)

(式中nは、0～70の整数である)

[Claim 3] An inorganic bulking agent consolidation polyester resin constituent given in either claim 1 characterized by obtaining the liquefied polybutene which has an epoxy group at the end from the liquefied polybutene of number average molecular weight 100-3,500, or claim 2.

[Claim 4] An inorganic bulking agent consolidation polyester resin constituent given in either claim 1 characterized by obtaining the liquefied polybutene which has an epoxy group at the end from the liquefied polybutene of number average molecular weight 200-1,400, or claim 2.

---

[Translation done.]

## \* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the inorganic bulking agent consolidation polyester resin constituent which improved reinforcement and hydrolysis-proof nature (heat-resistant aging nature).

[0002]

[Description of the Prior Art] When thermoplastic polyester carries out heating melting kneading with inorganic bulking agents, such as a glass fiber, it is known that the idle bulking agent combination resin constituent with which thermal resistance, such as reinforcement, such as tensile strength, and load deflection temperature, was improved substantially will be obtained. And if the approach of carrying out surface treatment of the inorganic bulking agents, such as a glass fiber, is learned for the silane system compound, the titanium system compound, etc. as an approach of heightening the amelioration effectiveness and a maleic-anhydride denaturation polyolefine wax is used together, heightening the amelioration effectiveness further is also known. However, these do not improve the hydrolysis-proof nature (heat-resistant aging nature) of polyester itself about the interaction of the interface between polyester/inorganic bulking agent. Since the end carboxyl group of polyester intramolecular is participating in hydrolysis, in order to improve the hydrolysis-proof nature (heat-resistant aging nature) of polyester, it is necessary to provide separate technical means.

[0003]

[Problem(s) to be Solved by the Invention] This invention tends to attain hydrolysis-proof nature (heat-resistant aging nature) amelioration of interaction adjustment of polyester / inorganic bulking agent interface, and polyester itself with a single means in view of an above-mentioned situation, and tends to offer the inorganic bulking agent consolidation polyester resin constituent excellent in reinforcement and hydrolysis-proof nature.

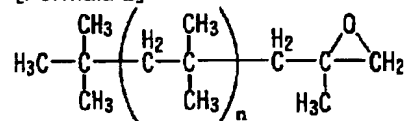
[0004]

[Means for Solving the Problem] This invention solves the above-mentioned technical problem by performing closure of the carboxyl group in polyester, and interaction adjustment of polyester / inorganic bulking agent interface by carrying out melting kneading of the epoxy group content liquefied polybutene of thermoplastic polyester, an inorganic bulking agent, and specific structure.

[0005] It is related with the inorganic bulking agent consolidation polyester resin constituent obtained by carrying out melting kneading of the liquefied polybutene 0.1 which has an epoxy group at the 1st thermoplastic polyester 95 - 55 weight sections of this invention, an inorganic bulking agent 5 - 45 weight sections (let both be the 100 in all weight sections.), and the end - the 5 weight sections.

[0006] It is related with the inorganic bulking agent consolidation polyester resin constituent characterized by being that in which more than 80 mol % of the liquefied polybutene which has an epoxy group at the end has the structure of a formula (1) in the 1st [ of this invention ] of the 2nd this invention.

[Formula 2]



式(1)

(式中 n は、0 ~ 70 の整数である)

[0007] It is related with the inorganic bulking agent consolidation polyester resin constituent with which liquefied polybutene which has an epoxy group at the end in the 1st [ of this invention ] of the 3rd this invention or the 2nd is characterized by being obtained from the liquefied polybutene of number average molecular weight 100-3,500.

[0008] It is related with the inorganic bulking agent consolidation polyester resin constituent with which liquefied polybutene which has an epoxy group at the end in the 1st [ of this invention ] of the 4th this invention or the 2nd is characterized by being obtained from the liquefied polybutene of number average molecular weight 200-1,400.

[0009]

[Embodiment of the Invention] Although there will be especially no limit if the polyester concerning <polyester> this invention is thermoplastic polyester, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyethylenenaphthalate (PEN), Poly 1, 4-cyclohexane dimethylene terephthalate (PCT), the thermoplastic polyester elastomer that makes these a hard segment and uses a polyether, amorphous polyester, etc. as a soft

segment, half-aromatic series liquid crystal polyester, and all aromatic series liquid crystal polyester are included preferably. That effectiveness is most acquired in these are crystalline polyester (PET, PBT, PCT, etc.) which makes a terephthalic acid and diol the main repeat unit. Especially a desirable thing is a thermoplastic polyester elastomer which makes PET and PBT, and these a hard segment, and uses a polyether, amorphous polyester, etc. as a soft segment from a viewpoint which avoids that melting kneading temperature becomes an elevated temperature too much, and its crystalline large polyester of especially the reinforcement effectiveness of an inorganic bulking agent is desirable.

[0010] The inorganic bulking agent concerning <inorganic bulking agent> this invention is an inorganic material blended in order to obtain a mechanical strength and mold goods excellent in thermal resistance, and is classified into the gestalt of the shape of the shape of fibrous and a particle, tabular, or hollow in the range which does not spoil the moldability of polyester, and a property. As a fibrous bulking agent, the fibrous object of metals, such as a glass fiber, an asbestos fiber, carbon fiber, a silica fiber, a silica alumina fiber, a zirconia fiber, a boron nitride fiber, nitriding silicon fiber, a boron fiber, titanite-acid potash fiber and also stainless steel, aluminum, titanium, copper, and brass, etc. is mentioned. As a particle-like bulking agent, the carbonate of the metal like carbon black, a silica, quartz powder, a glass bead, glass powder, calcium silicate, aluminum silicate, a kaolin, talc, clay, diatomite, the silic acid salt like wollastonite, ferrous oxide, titanium oxide, the oxide of the metal like an alumina, a calcium carbonate, and a magnesium carbonate, a calcium sulfate, the sulfate of the metal like a barium sulfate, other carbonization silicon, nitriding silicon, boron nitride, various metal powder, etc. are mentioned. As a tabular bulking agent, a mica, a glass flake, various metallic foils, etc. are mentioned. Moreover, as a hollow-like bulking agent, milt balun, metal balun, glass balun, etc. are mentioned. In this invention, especially a desirable inorganic bulking agent is a glass fiber or carbon fiber.

[0011] An inorganic bulking agent may carry out surface treatment using an organic silane, organic borane, organic titanate, etc. moreover, these inorganic bulking agents — one sort — or two or more sorts can be used together. Furthermore, a maleic-anhydride denaturation polyolefine wax can also be used together.

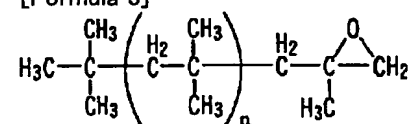
[0012] Let both be the 100 in all weight sections in this invention in the range of polyester 95 – 55 weight sections, and an inorganic bulking agent 5 – 45 weight sections. The amelioration effectiveness according that inorganic bulking agents are under 5 weight sections to an inorganic bulking agent is inadequate, and it injures fabricating-operation nature or toughness and is not desirable if 45 weight sections are exceeded.

[0013] The liquefied polybutene (henceforth "epoxy group content liquefied polybutene") which has an epoxy group at the end of a <epoxy group content liquefied polybutene> chain can carry out epoxidation of the end carbon and the carbon double bond in the chain of liquefied polybutene, and can obtain it. The liquefied polybutenes of a raw material are C4 fraction from FCC in petroleum refining, C4 fraction produced in disassembly of the hydrocarbon of naphtha and others, carry out the polymerization of an isobutylene, butene-1, the thing containing the butane other than a butene -2, or the thing that added the isobutylene etc. to C4 fraction and adjusted the presentation to it by Friedel-Crafts catalysts, such as an aluminum chloride and 3 boron fluoride, etc., and are obtained. The main configuration unit of liquefied polybutene originates in an isobutylene. Although carbon and a carbon double bond exist in the end of liquefied polybutene and the structure has a vinyl mold, a vinylidene mold, etc., for the object of this invention, a vinylidene mold is desirable. The manufacturing method of the liquefied polybutene which has such an end vinylidene radical is indicated by JP,10-306128,A etc.

[0014] Epoxy group content liquefied polybutene can be obtained by the well-known approach. For example, the method of a peracetic acid and sodium acetate being dropped and manufacturing epoxy group content liquefied polybutene is shown in JP,51-8966,B, stirring liquefied polybutene and n-hexane. Although the same approach is indicated by the Europe patent disclosure official report EP 045749, the U.S. Pat. No. 3,382,255 official report, etc., these approaches can also be used preferably.

[0015] In this invention, it is desirable that more than 80 mol % of epoxy group content liquefied polybutene is a bottom type (1).

[Formula 3]



式(1)

(式中nは、0～70の整数である)

Since the epoxy group content liquefied polybutene of a formula (1) does not have the 3rd class carbon atom substantially, it is excellent in heat-resistant degradation nature and anti-oxidation degradation nature, is stable also in the melting working temperature of polyester, and excellent also in long term stability. in addition, the structure concerned — more than 80 mol % — the well-known approach by which the included epoxy group content liquefied polybutene is indicated by JP,10-306128,A etc., for example, an isobutylene, — therefore, it is obtained by carrying out the polymerization of independent or the C4 fraction containing the butene-1 and butene-2 grade other than an isobutylene to the bottom of existence of a boron-trifluoride complex compound catalyst.

[0016] In this invention, it is desirable that epoxy group content liquefied polybutene is obtained from the liquefied polybutene of number average molecular weight 100–3,500 (number average molecular weight by GPC measurement (polystyrene reduced property)) within the limits. If volatility is too high and may vaporize at the time of stirring or melting, when number average molecular weight is less than 100, and 3,500 is exceeded, distribution within the

stirring system before melting kneading and/or diffusion within a melting kneading system, and reactivity are not enough, and the effectiveness of this invention may not fully be acquired. Furthermore, from distribution and diffusion of epoxy group content liquefied polybutene, and the point of the balance of surface preparation and reactivity (hydrolysis), number average molecular weight of liquefied polybutene is preferably made into within the limits of 100-1,400, and is made into within the limits of 100-900 still more preferably.

[0017] Since epoxy group content liquefied polybutene is low molecular weight compared with the polymer (for example, illustrated by JP,10-245475,A.) containing the usual oxirane radical (epoxy group), a polybutene chain is not concerned with the reaction of the epoxy group which has arranged in the top where diffusion is easy and has been arranged at the end within distribution within mixed stock, or a melting kneading system, and the carboxyl group in polyester as a steric hindrance factor. Therefore, epoxy group content liquefied polybutene can react easily with the carboxyl group in polyester, and the hydrolysis-proof nature of polyester can be raised, and the attached groundwater or finishing agent, and chemical interaction on the front face of an inorganic bulking agent can be produced in the same reason, and a packing effect increases.

[0018] In this invention, 0.1-5 weight section addition of the epoxy group content liquefied polybutene is carried out to the mixture 100 weight section containing polyester 95 - 55 weight sections, and an inorganic bulking agent 5 - 45 weight sections, and melting kneading is carried out. Effectiveness is not fully acquired in case of under the 0.1 weight section, but when 5 weight sections are exceeded, the problem of bleeding may be produced in mold goods. In addition, since the optimal mixed rate changes with compounding ratios of polyester and an inorganic bulking agent, it needs to select suitably within the limits of the above.

[0019] The epoxy group content liquefied polybutene concerning <mixing / kneading> this invention can be applied to easy for front faces, such as polyester system resin before melting kneading initiation, and homogeneity by diluting with warming or other solvents remaining as it is or if needed, since it is a liquid, and mixing with polyester system resin etc. with stirring mixers, such as a Henschel mixer and a tumbler mixer. In addition, epoxy group content liquefied polybutene may be added before melting of polyester, or to the back using natural dropping from the douche close to a kneading machine with a pump, or the vent-port of a kneading machine etc.

[0020] In case an inorganic bulking agent mixes epoxy group content liquefied polybutene and polyester, it may be made to live together, and it may be added from the halfway of a melting kneading process with a side feeder. Moreover, epoxy group content liquefied polybutene, coincidence, or separate any is sufficient as this addition. As long as there is no problem of the filamentation of a fibrous inorganic bulking agent etc., after making an inorganic bulking agent, epoxy group content liquefied polybutene, and polyester live together and mixing, it is desirable to perform melting kneading. When using a fibrous inorganic bulking agent, the approach of supplying to a screw via the process mixed gently with the mixed feeder (for example, thing which has a spiral-like screw.) which dropped into the kneading-machine hopper the polyester and the inorganic bulking agent which were mixed with epoxy group content liquefied polybutene from the separate quantum feeder, and connected them with the bottom of a hopper is the most desirable.

[0021] In this invention, more than the melting point of this polyester, thermoplastic polyester system resin and epoxy group content liquefied polybutene are desirable temperature higher 5-100 degrees C than the melting point and desirable temperature high 10-60 degrees C, and react easily by carrying out melting kneading especially. The thing for 20 seconds - 10 minutes to do for between melting kneading is desirable still more desirable, and mixing time is 40 seconds - 3 minutes especially preferably for 30 seconds to 5 minutes. It produces decomposition, an anomalous reaction, etc. of polyester and is not desirable if a reaction may not fully advance unless it fulfills the range of these temperature and time amount, and it exceeds.

[0022] In addition, in melting kneading, if a catalyst is used, the effectiveness of this invention can be heightened, in order to promote the reaction of epoxy group content liquefied polybutene and the carboxyl group of a polyester end, and the reaction of epoxy group content liquefied polybutene and an inorganic bulking agent surface layer. What is necessary is just to use as a catalyst what is generally used as a reaction of epoxy. For example, they are the metal salts of the periodic-table-of-the-elements I-a group of an amine compound, phosphorus compounds, ten or more carbon atomic numbers monocarboxylic acid, or dicarboxylic acid, or an II-a group. They are especially desirable trivalent phosphorus compounds, such as tributyl phosphoretted hydrogen triphenylphosphines. These may use two or more kinds together.

[0023] There is no limit in the device which carries out melting kneading in any way, and well-known devices, such as a Banbury mixer, a roll, a monopodium kneading extruder, and a biaxial kneading extruder, can be used for the melting kneading-machine machine and concrete target equipped with a heating facility. In addition, these devices did not necessarily need to be prepared into the device which manufactures a pellet, and could be prepared into the making machine of arbitration, such as monochrome or a multifilament manufacture machine, a container manufacture machine, a sheet manufacture machine, and an injection molding machine. The desirable method of acquiring the effectiveness of this invention is an approach of supplying one shaft or a biaxial extruder, carrying out melting kneading processing 1 minute or more preferably 30 seconds or more, and manufacturing a pellet, after mixing a predetermined component to homogeneity with a tumbler or a mixer like a Henschel mixer.

[0024] moreover — the case where carried out reduced pressure attraction with the vacuum pump etc. preferably the melting kneading in process of a kneading machine, and by preparing a clear aperture in a final process, and unreacted epoxy group content liquefied polybutene remains since, as for epoxy group content liquefied polybutene, it had volatility sufficient in the bottom of atmospheric pressure or reduced pressure in the melting kneading temperature of polyester — these — a part — or all can be removed out of a system and it is effective in property

stabilization of an end product.

[0025] As for the inorganic bulking agent consolidation polyester resin constituent of this invention, additives, such as an impact amelioration agent like an antioxidant, a thermostabilizer, an ultraviolet ray absorbent, lubricant, a nucleating additive, a plasticizer, a release agent, a pigment, and various elastomers, may be blended if needed. Therefore, the constituent obtained by blending components other than these with the liquefied polybutene which has an epoxy group at thermoplastic polyester, an inorganic filler, and the end, and carrying out melting kneading is included in the inorganic bulking agent consolidation polyester resin constituent of this invention.

[0026] (Example) Hereafter, although this invention is further explained in full detail by the example and the example of a comparison, this invention is not limited by these.

the end vinylidene structure acquired by the manufacture approach of <manufacture of epoxy group content liquefied polybutene> (example 1 of manufacture) JP,10-306128,A — 80-mol % — the mixture of a peracetic acid (40-% of the weight acetic-acid solution) and sodium acetate is dropped, putting in liquefied polybutene and n-hexane and stirring the liquefied polybutene (Mn=250) to contain in a cooling system, heating apparatus, and a reaction container with a dephlegmator, according to the approach of JP,51-8966,B. Performed accommodation of a dropping rate and cooling, and it was made to react at 20-30 degrees C, and stirred after dropping termination, subsequently the product was underwater poured out except for n-hexane by vacuum distillation, evaporation clearance of the ether was carried out through washing by an ether extract, water, and sodium carbonate, and desiccation, and the mixture which contains the liquefied polybutene which has an epoxy group at the end 70% of the weight was obtained. Hereafter, this is called "epoxy group content liquefied polybutene A."

[0027] (Example 2 of manufacture) The mixture which contains the liquefied polybutene which has an epoxy group at the end like the above-mentioned example 1 of manufacture 70% of the weight was manufactured using the liquefied polybutene (Mn=800) containing 80 mols of end vinylidene structures acquired by the manufacture approach of JP,10-306128,A. Hereafter, this is called "epoxy group content liquefied polybutene B."

[0028] After drying the polyethylene terephthalate chip 100 weight section of <manufacture of inorganic bulking agent consolidation polyester resin constituent> (example 1) intrinsic viscosity 0.9, it put into the drum tumbler, and 5 weight sections addition of the epoxy group content liquefied polybutene A was carried out, and it mixed. It continued, the polyethylene terephthalate chip covered with the epoxy group content liquefied polybutene A was fed into the hopper of the biaxial melting kneading machine of 46mm of diameters phi of a screw (ratio-of-length-to-diameter=36) with the belt type quantum feeder, and the glass fiber (6mm chopped strand) was supplied with the belt type quantum feeder from the vent-port of the downstream which polyester fused. the polyester at this time, and the ratio of a glass fiber — 70 weight sections: — since it considered as 30 weight sections, the addition of the epoxy group content liquefied polybutene A to both sum 100 weight section became the 3.5 weight sections. Melting kneading was carried out by barrel maximum-temperature 280 \*\*, and it pelletized at the process which extrudes and carries out water cooling and which is omitted from a dice. Moreover, the open vent-port was prepared near the dice, the vacuum pump was operated, and volatile matter was removed. Moreover, it was 40 seconds when the time amount by which a charge pellet is conveyed by the screw from under a hopper, and is extruded from a dice was measured with the color pellet.

[0029] (Example 2) After drying the polybutylene terephthalate pellet (Jura NEKKUSU 2000: polyp lastic company make) 100 weight section, it put into the drum tumbler, and 5 weight sections addition of the epoxy group content liquefied polybutene B was carried out, and it mixed. It continued, the polyethylene terephthalate pellet covered with the epoxy group content liquefied polybutene B was supplied to the hopper of the biaxial melting kneading machine of 46mm of diameters phi of a screw (ratio-of-length-to-diameter=36) with the belt type quantum feeder, and the glass fiber (chopped strand with an average die length of 6mm) was supplied with the belt type quantum feeder from the vent-port of the downstream which polyester fused. the polyester at this time, and the ratio of a glass fiber — 70 weight sections: — since it considered as 30 weight sections, the addition of the epoxy group content liquefied polybutene B to both sum 100 weight section became the 3.5 weight sections. Melting kneading was carried out by barrel maximum-temperature 260 \*\*, and it pelletized at the process which extrudes and carries out water cooling and which is omitted from a dice. Moreover, the open vent-port was prepared near the dice, the vacuum pump was operated, and volatile matter was removed. Moreover, it was 40 seconds when the time amount by which a charge pellet is conveyed by the screw from under a hopper, and is extruded from a dice was measured with the color pellet.

[0030] (Example 1 of a comparison) In the example 1, the pellet was obtained like the example 1 except having not added epoxy group content liquefied polybutene.

(Example 2 of a comparison) In the example 2, the pellet was obtained like the example 2 except having not added epoxy group content liquefied polybutene.

[0031] The test piece for tension tests based on ASTM/D638 in a 40mm [/second] injection speed, injection-pressure 700kgf/cm<sup>2</sup>, and injection time amount 10 seconds considering the cylinder temperature of the injection molding machine of 60t of <shaping of test piece> (example 1 and example 1 of comparison) clamping pressure as 250 degrees-C [ of backs ], 260 degrees-C [ of CHUBU ENGINEERING CORPORATION ], 260 degrees-C [ of anterior part ], and nozzle 260degree C was fabricated. The die temperature was made into 70 degrees C, and cooldown delay 15 seconds.

(An example 2 and example 2 of a comparison) The test piece for tension tests based on ASTM/D638 in a 40mm [/second] injection speed, injection-pressure 700 kgf/cm<sup>2</sup>, and injection time amount 10 seconds considering the cylinder temperature of the injection molding machine of 60t of clamping pressure as 210 degrees-C [ of backs ],

220 degrees-C [ of CHUBU ENGINEERING CORPORATION ], 240 degrees-C [ of anterior part ], and nozzle 240degree C was fabricated. The die temperature was made into 50 degrees C, and cooldown delay 15 seconds. [0032] The relative value estimated the tensile strength of each test piece after carrying out predetermined time immersion at 100-degree-C simmering heat water in an autoclave, using initial tensile strength (ASTM/D638) of the example of a <hydrolysis-proof [ tensile strength and ] nature assessment> comparison as 100. A result is shown in a table 1 and a table 2. It has checked that the reinforcement and hydrolysis-proof nature of the inorganic bulking agent consolidation polyester resin constituent concerning this invention were improved from the result shown in a table 1 and a table 2.

[0033]

[A table 1]

ガラス繊維強化ポリエチレンテレフタレート樹脂の引張強さの相対値

組成物	初期値	浸漬 2 4 時 間後	浸漬 4 8 時 間後	浸漬 7 2 時 間後
比較例 1	1 0 0	9 5	9 1	8 1
実施例 1	1 0 5	1 0 0	9 5	9 0

[0034]

[A table 2]

ガラス繊維強化ポリブチレンテレフタレート樹脂の引張強さの相対値

組成物	初期値	浸漬 2 4 時 間後	浸漬 4 8 時 間後	浸漬 7 2 時 間後
比較例 2	1 0 0	9 6	9 2	8 2
実施例 2	1 0 8	1 0 2	9 8	9 4

[0035]

[Effect of the Invention] According to this invention, the inorganic bulking agent consolidation polyester resin constituent excellent in reinforcement and hydrolysis-proof nature can be offered.

---

[Translation done.]